STUDY OF α-ALKYLACRYLONITRILES

BY

WILLIAM RIEDEL MILLER

B.S., Iowa State College, 1946
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

Polyacrylonitrile is a very hard, insoluble polymer which resists virtually all organic solvents. Copolymers with acrylonitrile tend to take on the characteristics of this monomer to a greater or less extent. Studies have shown that copolymers of acrylonitrile with various methyl-substituted butadienes have the property of oil resistance. It would be of interest to investigate the properties of copolymers of butadiene with alkyl-substituted acrylonitriles with a view to the possible formation of a good oil-resistant rubber.

The only α-alkylacrylonitrile which is available is methacrylonitrile. Some syntheses of higher homologs have been advanced but they utilize methods which throw definite doubt on the purity of the compounds.

An excellent and apparently unequivocal method of preparing α-alkylacrylonitriles was presented by the availability of α-alkylacroleins (1). Preparation and dehydration of the oximes of these acroleins should give the desired α-alkylacrylonitriles without question as to the location of the double bond.

It was the purpose of this investigation to examine these reactions and to prepare and characterize a series of α-alkylacrylonitriles.

Discussion of Results

Four α-alkylacrylonitriles were prepared by the dehydration of the oximes of the corresponding α-alkylacroleins and these nitriles have been characterized. The alkyl substituents were ethyl, isopropyl, *n*-amyl, and *n*-hexyl.

The acroleins from which these nitriles were prepared were made by the application of the Mannich reaction as developed by Marvel, Myers and Saunders (1). The reaction

was further extended to the preparation of α-*n*-hexylacrolein from *n*-octyl aldehyde and α-*n*-octylacrolein from *n*-decyl aldehyde.

The oximes were prepared by the addition of a solution of sodium carbonate to a mixture of the substituted acrolein with a solution of hydroxylamine hydrochloride. The oximes so prepared are very viscous liquids which are purified by distillation. The conditions of the distillation must be very carefully regulated as the oximes tend both to polymerize and decompose when heated.

The oximes were dehydrated by refluxing with acetic anhydride. The dehydration of the ethyl homolog was carried out essentially in the manner described by Mowry and Morner (2): The reaction mixture is slowly distilled, neutralized, extracted and redistilled. The other homologs were separated from the neutralized reaction mixture by steam distillation.

The α-alkylacrylonitriles are relatively stable compounds which gave analyses which were in good agreement with the calculated values. The α-isopropylacrylonitrile is the least stable of the nitriles prepared.

Preliminary experiments indicate that these α-alkylacrylonitriles are not readily polymerized under conditions which will polymerize methacrylonitrile.

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VITA

The author was born on November 3, 1923, in Cedar Falls, Iowa. After graduating from Cedar Falls High School in 1941, he entered the Iowa State College. From 1944 to 1946 he served in the Army of the United States. Upon discharge from the Army he returned to the Iowa State College and received his Bachelor of Science degree in December, 1946. He entered the Graduate College of the University of Illinois in September, 1947, and received the Master of Science degree in August, 1948. He held a Teaching Assistantship from September, 1947, to August, 1949, and a University Fellowship in the academic year 1949-50.